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CLAUSIUS-MOSSOTTI FUNCTION FOR RESTRICTED
ONE-DIMENSIONAL OSCILLATORS

by

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ABSTRACT

Deviations from constancy of the C_M function, are considered on the basis of a one-dimensional oscillator model in which the valence electrons are assumed restricted by infinite potentials, but interact with all others through dipolar forces.

A computer calculation shows that the density-dependence of C_M is qualitatively in agreement with experiment, but the temperature-dependence is negligible.

An interesting feature is the occurrence of *negative* polarizabilities for the excited states at modest densities - indicating an insulator-to-metal transition. This result is in conflict with the basic precepts of the model which does not permit fully delocalized electronic states.

However, this analysis suggests a more promising three-dimensional model which admits of realistic atomic potentials, dynamical dipolar interaction and repulsive potentials which ensure the existence of the ionized state of the atom.

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I INTRODUCTION

Experiments carried out over the past fifty years have established the form of the Clausius-Mossotti function, C_M as a function of density and temperature for many gases (see the excellent review article by Sutter, [1]). In almost all cases, as the density increases C_M at first increases, goes through a maximum at a few hundred amagats, and thereafter decreases with increasing density.

There are, however, some important exceptions to this general rule; namely, the C_M -functions for He, Ne and possible H_2 . In He, C_M actually *decreases* with increasing density at *low* densities as well as high ones and no maximum occurs in the whole density range 100-900 amagats, Vidal, *et al*, [2]. In Ne, $dC_M/d\rho$ is also negative at low densities with a slope about 5 times greater than that for He, Orcutt and Cole [3]. For H_2 , Michels, *et al*, [4], found $dC_M/d\rho \approx 0$ within their range of experimental error; but Orcutt and Cole *loc cit* reported that at low densities $dC_M/d\rho > 0$ (with a small magnitude numerically about equal to that of He).

Theories to account for the deviations of C_M from constancy are, generally, one of two types:

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(a) *Statistical Theories* in which the polarizability of the particle is treated as constant, but where the medium surrounding it experiences density fluctuations.

(b) *Continuum Theories* which ignore fluctuations, but in which the polarizability of an individual particle depends on the mean density of the surrounding medium.

Theories of the first type were initiated by Yvon, [5], and Kirkwood, [6], while those in the second category commenced with the work of Michels, *et al*, [7], and Ten Seldam, and de Groot, [8]. Some theories; e.g., Mazur, [9], combine the two approaches, but in general no theory has been able to account for all the experimental results observed for typical nonpolar gases over wide ranges of density and, to the authors' knowledge, no theory has yet been developed which accounts for the negative, low density values of $dC_M/d\rho$ observed in the exceptional gases He and Ne.

The main object of the present paper is to point out a fundamental deficiency in existing theories, namely; the neglect of a *finite* activation energy for the valence electrons and the consequent neglect of the delocalized electronic states and their ability to screen the interparticle dipolar forces.

3.

To illustrate how this oversight can completely change the conceptual basis of theories for the C_M function, we consider here a very simple model of a one-dimensional harmonic oscillator which is restricted by infinite potential barriers, (arising from the finite density of the surrounding medium) but which interact with all others in the ensemble through long-range, dipolar forces. The present theory is of the "continuum type" so that changes in C_M are proportional to changes in the polarizability of the individual particle, and it is found that the calculated ground state polarizabilities lead to C_M functions in qualitative agreement with experiment for typical gases such as Ar, Kr, N₂ and CO₂. These results are valid, strictly speaking, only at $T = 0^\circ\text{K}$. However, if one seeks the temperature dependence of C_M it is necessary first to calculate the polarizabilities of the excited electronic states since when $T > 0^\circ\text{K}$ not all electrons will be in the ground state. Here a surprising result occurs, namely; that at quite *modest* densities (several hundred amagats), easily achieved experimentally, the computed polarizabilities of the excited states can become *negative*. This result may be interpreted to mean that electrons in these

4.

levels have become de-localized through the well-known mechanism of the dielectric catastrophe which occurs when the particle density is sufficiently high that the attractive dipolar forces overcome the binding forces of the electron to its core.

At $T > 0^{\circ}\text{K}$ the model thus breaks down completely since the possibility of the free electronic state occurring at modest densities was not considered at the outset. In this way we are reminded of the important omission of the existence of a finite activation energy in the present model and in others.

II THE ONE-DIMENSIONAL MODEL

To circumvent difficulties of inhomogeneous reaction fields and divergencies occurring in three-dimensional models (see §V) we first concentrate attention on a very simple model of a linear dipole which, in isolation, has a frequency ω_0 and whose fixed positive charge q is at the origin with its negative charge, $-q$ free to move in the x -direction. We imagine this dipole located in a plane slab of dielectric constant unity and with walls at $x = \pm x_0$. The regions $|x| > x_0$ we take to represent the "surrounding medium" of permittivity, ϵ .

5.

If E is a uniform macroscopic field in the x -direction at $|x| = \infty$, the field in the slab is homogeneous and given by $F = \epsilon E = E + 4\pi P$ where $P = -qN_0x$ is the dipole moment per unit volume. Here N_0 is the number density of (like) oscillators in the medium. The energy required to polarize the dipole is

$$W_p = q \int_0^x F(x') dx' = qEx - \frac{1}{2} m \omega_p^2 x^2 \quad (1)$$

where $\omega_p = (4\pi N_0 q^2 / m)^{\frac{1}{2}}$ is the plasma frequency of the bound charges, $-q$ in the medium. Thus taking account of the back-reaction of the medium, the effective potential energy of the oscillator is

$$V = \frac{1}{2} m \omega_{eff}^2 x^2 + qEx \quad (2)$$

where

$$\omega_{eff}^2 = \omega_0^2 - \omega_p^2 \quad (3)$$

is the density-dependent frequency of the

6.

oscillator in interaction with its surroundings. Clearly the equation of motion corresponding to (2) leads, for static fields, to the Clausius-Mossotti function

$$C_M^0 = \frac{\epsilon_s - 1}{3\epsilon_s} \left(\frac{W}{\rho} \right) = \frac{4\pi}{3} A \alpha_0 \quad (4)$$

where ϵ_s is the static dielectric constant, ρ the mass-density, W the molecular weight, $A = 6.02 \times 10^{23}$ is Avogadro's number and $\alpha_0 = e / m\omega_0^2$ is the polarizability of the isolated oscillator.

Let us now imagine that the walls at $x = \pm x_0$ are characterized by infinite potentials for $|x| \geq x_0$. The oscillator is then confined to the region $-x_0 \leq x \leq x_0$ and experiences both long-range, dipolar forces and short-range forces. In the absence of a macroscopic field the dimensionless Schrödinger equation for the charge, $-q$ is

$$-\frac{d^2\psi}{dy^2} + V(y)\psi(y) = w\psi(y) \quad (5)$$

7.

where

$$V(y) = \begin{cases} \frac{1}{2}y^2\left(1 - \frac{\omega_p^2}{\omega_0^2}\right) & : -y_0 \leq y \leq y_0 \\ 0 & : |y| > y_0 \end{cases}$$

In (5) we have introduced the dimensionless coordinate $y = (2m\omega_0/\hbar)^{\frac{1}{2}}x$ and dimensionless energy $w = W/\hbar\omega_0$. Here $(\hbar/2m\omega_0)^{\frac{1}{2}}$ is, essentially, the de Broglie wavelength of the isolated oscillator. In (5), $\psi(y)$ must be solved subject to the boundary condition

$$\psi(y_0) = \psi(-y_0) = 0 \quad (6)$$

The computer program which solves (5) subject to (6) is too long to present here. Full details may be found in the thesis by Tjipto Margo, [10]. For present purposes it

is sufficient to state that wave-functions and energies for the first 8 oscillator states ($n = 0, 1 \dots 8$) are on file for the gases Ar, Kr, N₂ and CO₂.

Values of ω_0 were found by extrapolating experimental C_M functions to zero density giving, in units of 10^{16} Hz, for Ar : $\omega_0 = 1.243$ for Kr : $\omega_0 = 1.009$; for N₂ : $\omega_0 = 1.220$; and for CO₂ : $\omega_0 = 0.924$. The connection between density and cavity thickness was taken to be

$$N_0 = \frac{1}{(2\kappa_0)^3} \quad (7)$$

and y_0 values were assumed in the range $2.5 \leq y_0 \leq 5$. This thickness range corresponds to density ranges (in amagats) for Ar : 1166 - 146; for Kr : 853 - 107; for N₂ : 1134 - 142 and for CO₂ : 748 - 93.5. For simplicity we also assumed $q = e = \text{electron charge}$.

III GROUND STATE POLARIZABILITY

The polarizability of the restricted oscillator experiencing dipolar interaction is

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found treating the energy $H' = qEx(E \rightarrow 0)$ as a perturbation. The ground state polarizability is then

$$\frac{\alpha^{(0)}}{\alpha_0} = \sum_{n=1} \frac{|\langle \psi_n(y) | y | \psi_0(y) \rangle|^2}{w_n - w_0} \quad (8)$$

where eight terms in (8) gives results to five significant figures. The C_M function is now given by

$$C_M = C_M^0 \left(\frac{\alpha^{(0)}}{\alpha_0} \right) \quad (9)$$

where C_M^0 is given by (4). The results for $\alpha^{(0)}/\alpha_0$ are shown in Fig. 1 for the gases under consideration. At low densities $dC_M/d\rho > 0$ because of the increasing importance of the dipolar forces as density is raised. However, at high densities the oscillator is so restricted that its energy level spacing is

10.

increased as density is raised - resulting in $dC_M/d\rho < 0$. The maxima in Fig. 1 occur at about the right densities for these gases, but in all cases $|dC_M/d\rho|$ is larger at both low and high densities than observed experimentally.

IV TEMPERATURE DEPENDENCE OF C_M AND POLARIZABILITIES OF EXCITED LEVELS

The temperature dependence of C_M may be calculated assuming the medium is a mixture of nonpolar oscillators with polarizabilities $\alpha^{(n)}$ and number densities $N^{(n)} = (N_0/\sigma) \exp(-\beta W_n)$ where $\sigma = \sum_{n=0} \exp(-\beta W_n)$ is the partition function. Assuming the same local field, F for all states leads at once to

$$C_M = \frac{4\pi}{3} A \langle \alpha(T) \rangle \quad (10)$$

where

$$\langle \alpha(T) \rangle = \frac{\sum_{n=0} \alpha^{(n)} \exp[-\beta(W_n - W_0)]}{\sum_{n=0} \exp[-\beta(W_n - W_0)]} \quad (11)$$

yields the average polarizability at temperature T . Apart from noting that $\langle \alpha \rangle$ has a negligible, negative temperature coefficient we do not calculate (10) since $W_n - W_0$ is so large compared to $kT (= \beta^{-1})$ that $\langle \alpha \rangle$ reduces to $\alpha^{(0)}$ at all temperatures. This result emphasizes the limitations of the oscillator model for calculating any property associated with excited levels. The difficulty is that the potential function of an oscillator is *concave* whereas that of a real atom is *convex*. The latter results in energy levels which cluster together at high principal quantum numbers whereas those of an oscillator do not.

Nevertheless, for the sake of completeness, we calculated the polarizabilities of the excited levels. These are given by

$$\frac{\alpha^{(n)}}{\alpha_0} = \sum_{n' \neq n} \frac{|\langle \psi_{n'}(y) | y | \psi_n(y) \rangle|^2}{w_{n'} - w_n} \quad (12)$$

and are shown in Fig. 2 for argon, and in Fig. 3 for CO₂. As mentioned in §I, the fact that $\alpha^{(n)}$ can become negative at *modest* densities indicates that at densities, ρ_n such that $\alpha^{(n)}(\rho_n) = 0$ the level n does not exist since, if occupied, the electron would be a free particle - in conflict with the assumption of an infinite activation energy which precludes the existence of fully delocalized states.

Clearly for any model there should always be a finite potential barrier for the valence electron(s) and as density is increased the strong overlap of potentials of neighbouring atoms would decrease the barrier height so that wave functions, energies and polarizabilities would be different from those calculated assuming an infinite activation energy. In addition, there should be a finite number, N of excited levels possible at any

given density and one may argue that N and the barrier height should be self-consistent with the *non*-appearance of negative polarizabilities for all bound states. With such a model dipolar forces between atoms or molecules would be screened by the existence of a finite density of free electrons resulting in a slower change of C_M with increasing particle density than in theories which ignore the possibility of delocalized electronic states. As may be seen, the above argument alters the conceptual basis for the calculation of C_M .

V FUTURE PROPOSALS

The present model is unsatisfactory in that it is:

- (a) one dimensional
- (b) unsuitable for calculating properties associated with excited states
- (c) lacks a finite activation energy.

A better model must start with a correct form for the atomic potential, $V_a(r)$ for the valence electron of the isolated atom. $V_a(r)$ will generally be coulomb or screened-coulomb with screening provided by the other atomic

electrons. This atom may then be thought of as being in a vacuum-filled sphere of radius a with its fixed core charge, e at the origin and electron, $-e$ at $0 \leq r \leq a$. If ϵ is the permittivity of the medium surrounding the sphere, it is then a straightforward matter to calculate the classical self-energy of the extended, atomic dipole in its own reaction field; viz,

$$V_{\text{self}} = -\frac{e^2}{a} \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) \sum_{n=1}^{\infty} B_n(\epsilon) \left(\frac{r}{a} \right)^{2n} \quad (13)$$

where

$$B_n(\epsilon) = \frac{(n+2)(2\epsilon+1)}{2[(n+2)\epsilon + n+1]}$$

It may be observed that, as expected,

(13) diverges at $r=a$ since at the surface the electron and its image charge are infinitely close. We may also note for all $1 \leq \epsilon \leq \infty$, and all $1 \leq n \leq \infty$ that $0.75 \leq B_n(\epsilon) \leq 1$ and there is little error in assuming as a good approximation that $B_n = 1$ in which case (13) becomes

$$V_{\text{self}} = -\frac{e^2}{a} \left[\frac{\frac{4\pi}{3} N_0 \alpha_0}{1 + \frac{4\pi}{3} N_0 \alpha_0} \right] \frac{(r/a)^2}{1 - (r/a)^2} \quad (14)$$

where, as a further good approximation, we have used the "unrefined" Clausius Mossotti formula to replace the factor $(\epsilon-1)/(2\epsilon+1)$ in (13) by the factor in [...] in (14).

The potentials $V_a(r)$ and $V_{\text{self}}(r)$ are shown in Fig. (4) as lines and their sum as the line ----. This sum clearly has a maximum, V_{max} at $r = r_{\text{max}} < a$. It is now required to add a repulsive potential such that continuous states of the electron are possible. The simplest way to accomplish this so that the total potential is monotonically increasing is to assume a repulsive energy:

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$$V_{rep} = \begin{cases} 0 & : 0 \leq r \leq r_{max} \\ -(V_a + V_{self} - V_{max}) & : r_{max} \leq r \leq a \\ 0 & : r > r_{max} \end{cases} \quad (15)$$

as shown by the line $\cdots\cdots\cdots$ in Fig. 4. The total potential is then

$$V(r) = \begin{cases} V_a(r) + V_{self}(r) & : 0 \leq r \leq r_{max} \\ V_{max} & : r_{max} \leq r \leq \infty \end{cases} \quad (16)$$

and is indicated in Fig. 4 by the hatched line.

Fig. 4 may be taken to represent the situation at some intermediate density, but as density increases V_{max} would increase and r_{max} , and the activation energy, $A_{N,L}$ would decrease, but the energy levels $E_{n,l}$ would begin to rise above their values in the

isolated atom. For sufficiently low densities free electron screening will be unimportant but as the density is raised and $A_{N,L}$ continues to decrease there will come a point, probably rather suddenly, at which sufficient free electrons will exist at ordinary temperatures that screening of the interatomic, dipolar forces will be significant. This point may occur when the screening radius $r_s = (\epsilon kT / 4\pi N_e e^2)^{1/2}$ is of the same order of magnitude as the dielectric radius $a = (3/4\pi N_0)^{1/3}$. Here the electron density, N_e may be calculated from the mass-action law

$$\frac{N_e^2}{N_0 - N_e} = \left(\frac{2\pi m^* kT}{h^2} \right)^{3/2} \sigma_{N,L}^{-1} \exp(-\beta A_{N,L}) \quad (17)$$

where N_0 is the density of centres and

$$\sigma_{N,L} = \sum_n^N \sum_l^L g_{n,l} \exp(-\beta E_{n,l})$$

is the partition function of the bound electrons corresponding to maximum principal and orbital quantum numbers N and L . In (17) the free electron mass, m^* may be larger than m if there are a large number of bound states with energies just below the continuum level.

When screening becomes important, the self-energy (14) must be modified and, as shown by Frood, [1], the polarizabilities, $\alpha^{(n,l)}$ of each bound state (n,l) together with the number density, $N^{(n,l)}$ of electrons in that level must be non-catastrophic; i.e.

$$1 - \alpha^{(n,l)} f^{(n,l)} \geq 0 \quad (18)$$

where

$$f^{(n,l)} = \frac{4\pi}{3} \cdot \frac{2(\epsilon-1)}{2\epsilon+1} N_0^{(n,l)}$$

is the reaction field factor for the level (n, ℓ) . When equality holds, (18) determines the maximum quantum numbers $N(\rho, T)$ and $L(\rho, T)$ which can exist at a given temperature and density.

A computer calculation based on the above model in which at each temperature and density the activation energy, $A_{N,L}(\rho, T)$ the number of excited states, $N(\rho, T)$ the free electron density, $N_e(\rho, T)$ and the permittivity, $\epsilon(\rho, T)$ are all mutually self-consistent would be of interest.

The foregoing remarks are closely connected with the possible appearance at high densities of the metallic state. Experimentally, it may thus be of interest to examine dielectric and/or conduction losses in very dense nonpolar gases as well as the static, or low-frequency C_M function.

VI LOW DENSITIES

At low densities $A_{N,L}$ will tend to I_0 (the ionization potential of the isolated atom), and (17) ensures that at ordinary temperatures there are too few free electrons for static screening to be possible. At such densities $r_{\max} \approx a$, where a is the dielectric radius, and $V_{\max} \approx e^2/a$ increases as the $\frac{1}{3}$ power of the density.

As density increases all energy levels will begin to rise above their values in the isolated atom because of the increase in $V_{\text{self}}(r)$, but more and more excited levels will become catastrophic. Thus the ground state polarizability will tend to increase from the first of these effects, but decrease because of the second.

In He and Ne, which have small incipient polarizabilities and where all excited levels are closer to the continuum than in ordinary gases, this may mean that the decrease of ground state polarizability due to catastrophes in the excited levels will be greater than its increase arising from the "broadening" of its effective potential $V(r) = V_a(r) + V_{\text{self}}(r)$ in (16). In this way C_M may be found to decrease with increasing densities for He and Ne at low densities.

The opposite situation should then pertain for "ordinary" gases; e.g., Ar and Kr, in that the increase in polarizability due to $V_{\text{self}}(r)$ should more than compensate its loss due to catastrophes in excited levels - resulting in a C_M which increases with density at low densities. Only detailed calculations for specific gases using the catastrophe criterion, (18) rather than the simple potential-overlap ($V_{\text{max}} \approx e^2/a$) can verify these possibilities.

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FIGURE CAPTIONS

- Fig. 1 Ground State Polarizabilities of the
One Dimensional Oscillator Model for Ar, Kr, N₂
and CO₂.
- Fig. 2 Polarizabilities of Excited States of
One Dimensional Oscillator Model for Ar.
- Fig. 3 Polarizabilities of Excited States of
One Dimensional Oscillator Model for CO₂.
- Fig. 4 Potential Function of Valence
Electron in Interaction with the
Surrounding Medium.

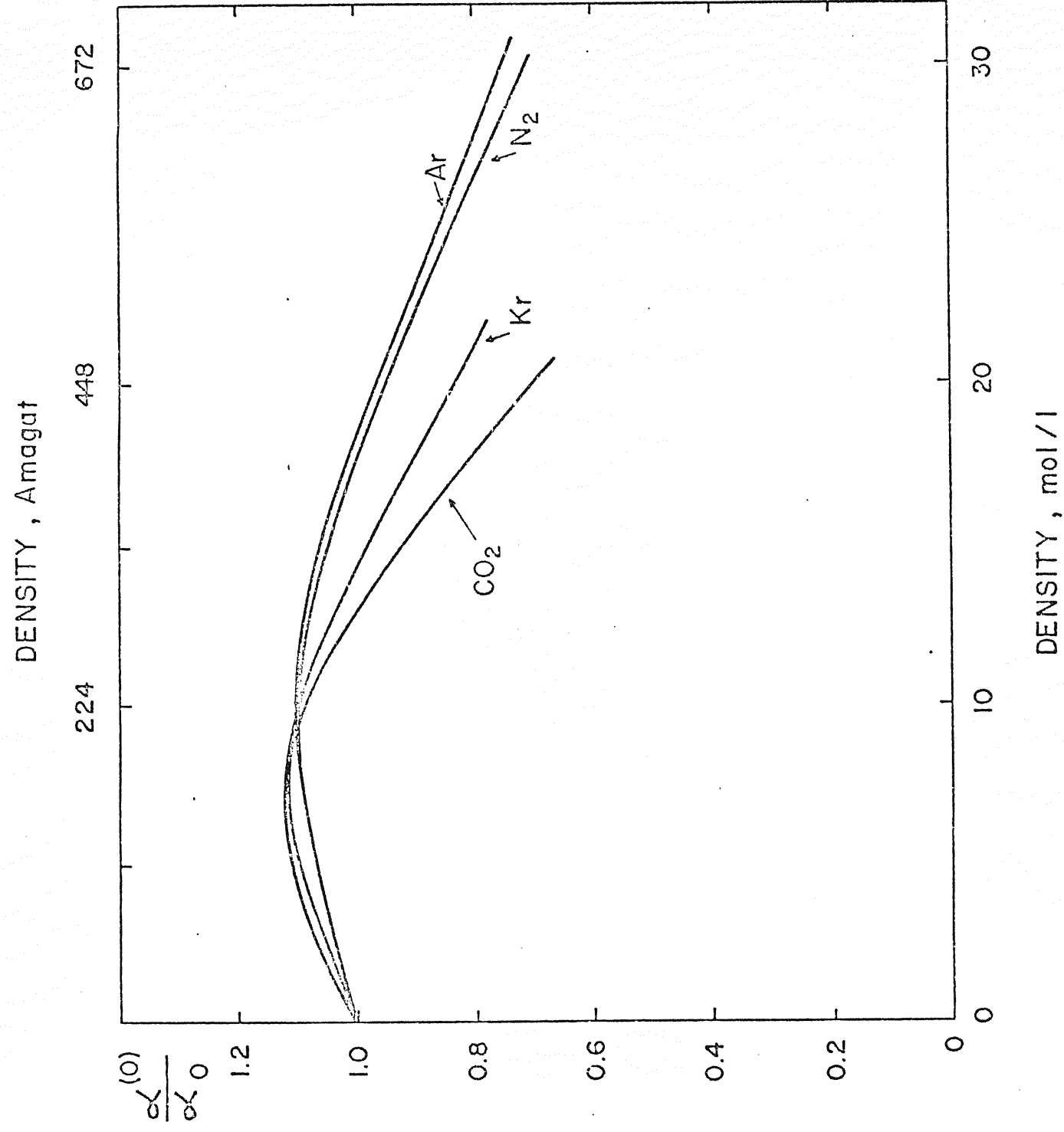


FIG. 1

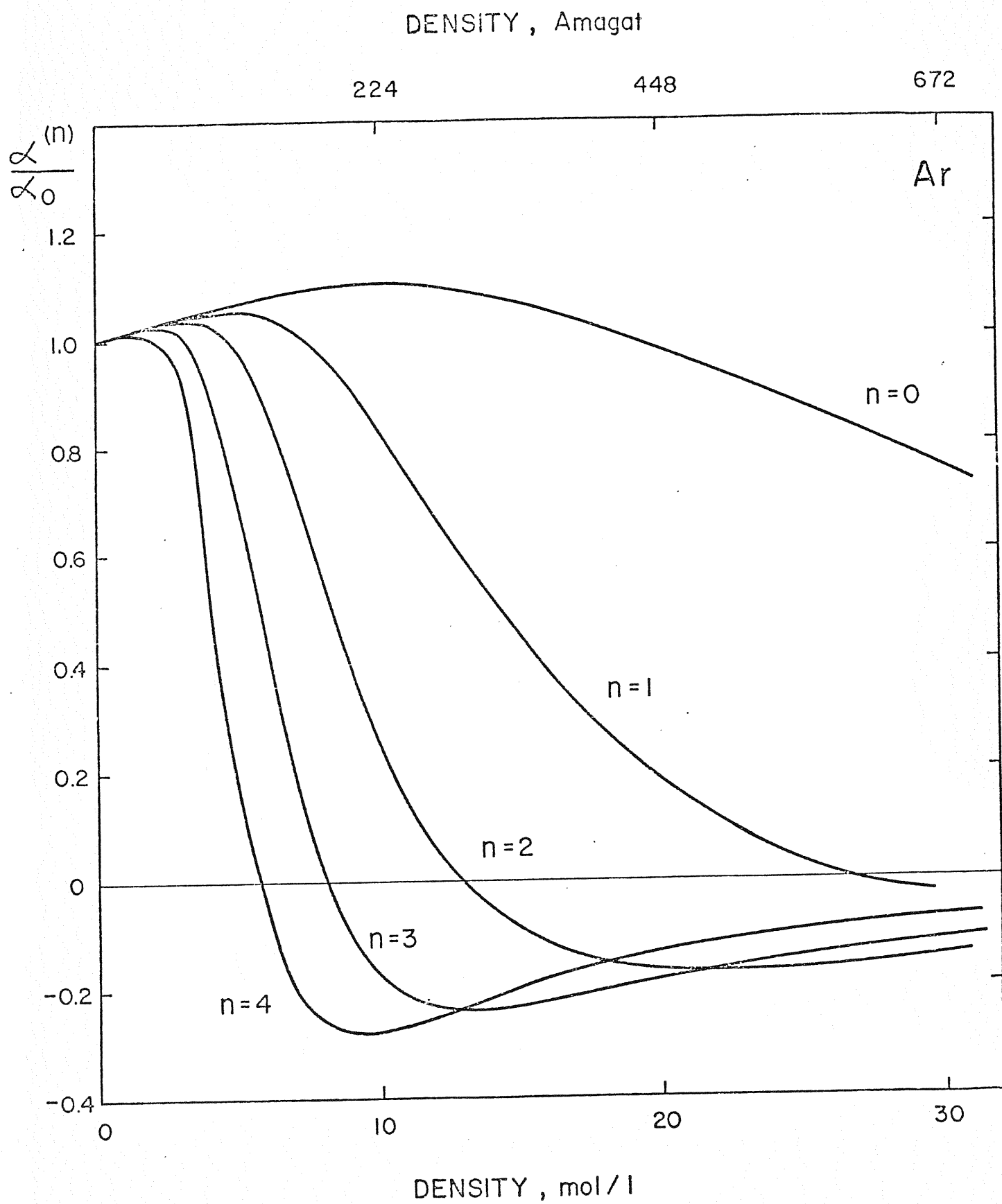


FIG. 2

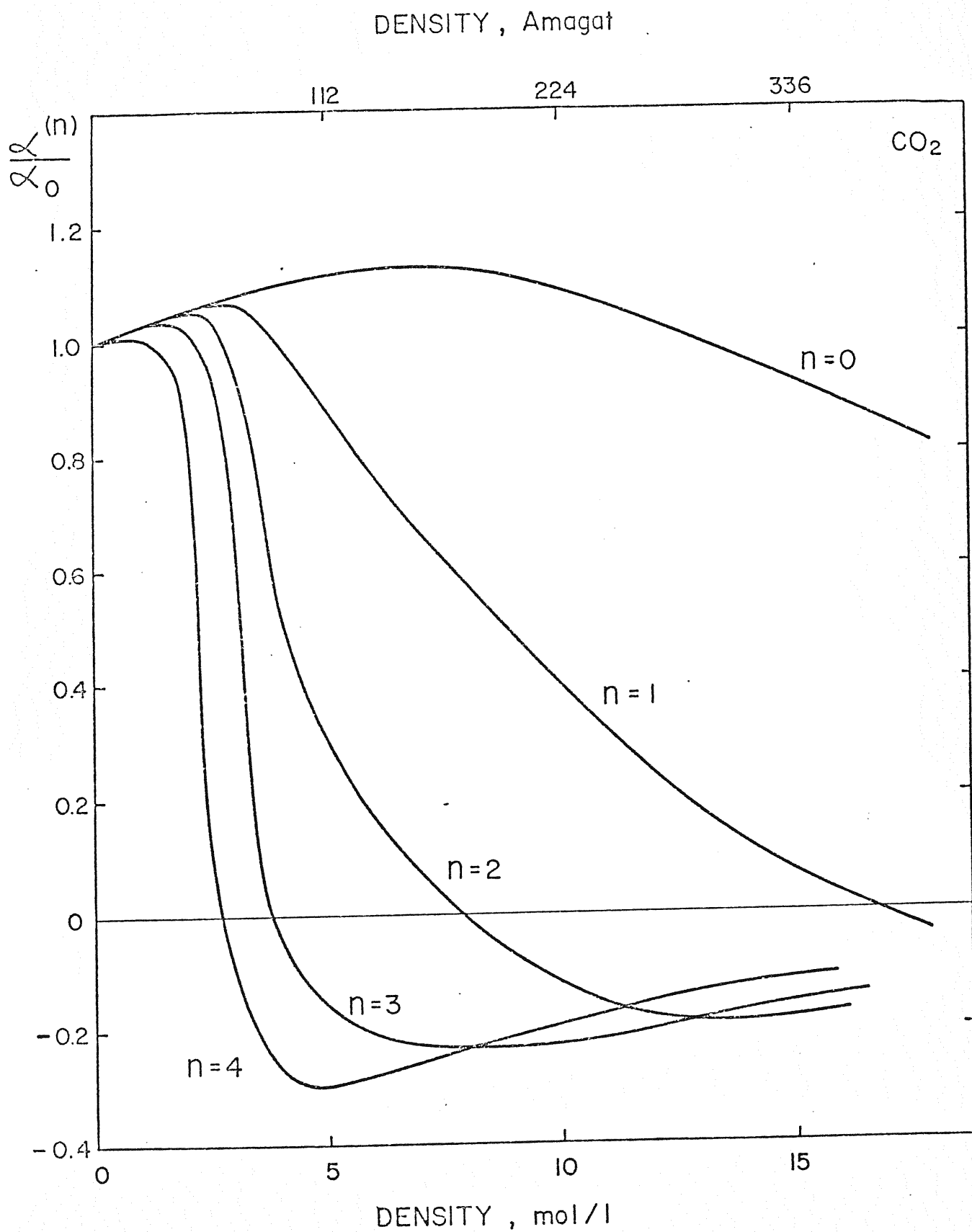


FIG. 3

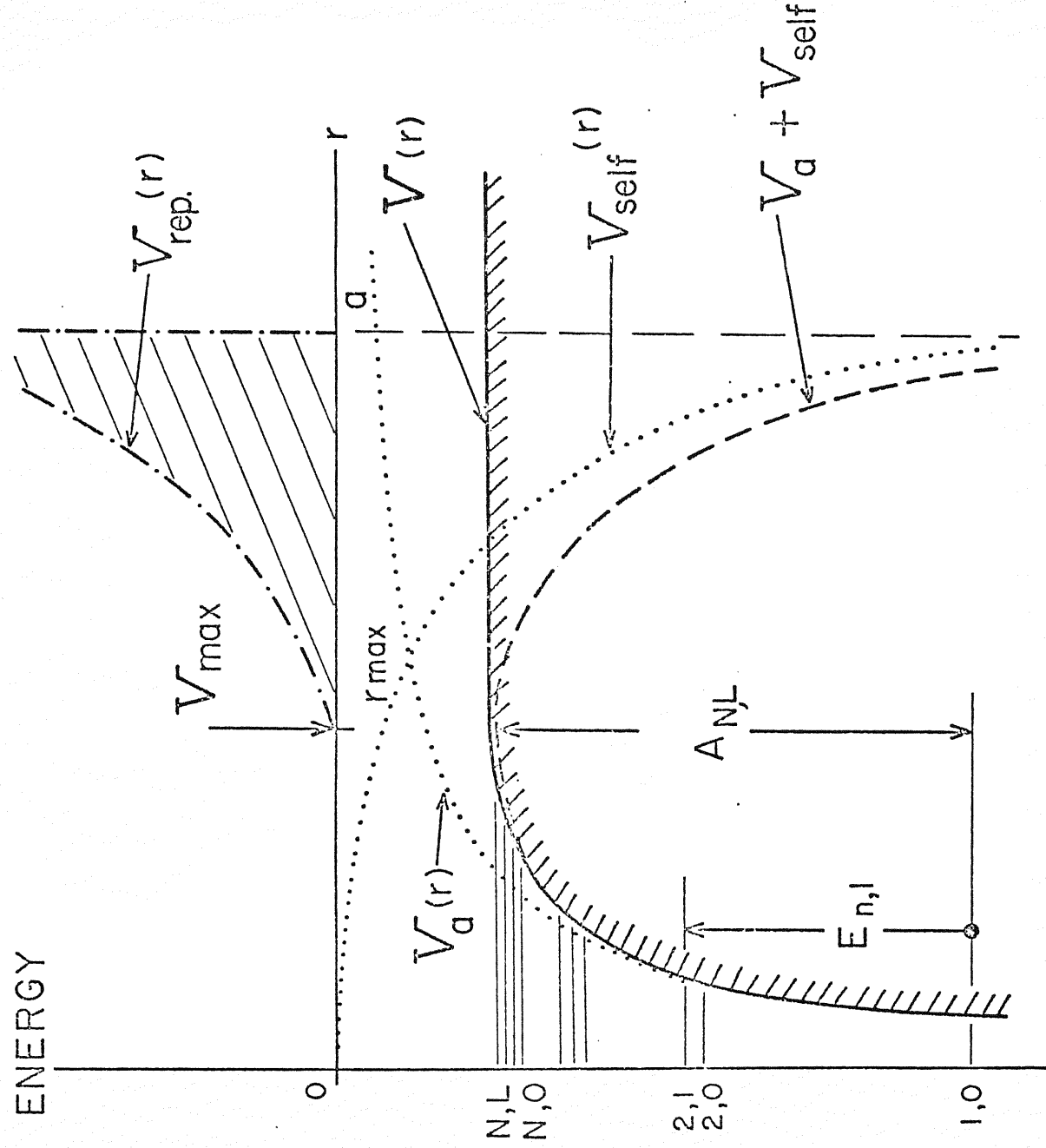


FIG. 4